

UDC 666.762.63

## CERAMICS BASED ON STRONTIUM ZIRCONATE (A REVIEW)

E. A. Slonimskaya<sup>1</sup> and A. V. Belyakov<sup>1</sup>

Translated from *Steklo i Keramika*, No. 2, pp. 18–20, February, 2001.

The paper reviews the available published information regarding the synthesis of strontium zirconate and the properties and application areas of ceramics based on this compound. The review also draws attention to the difficulties arising in using this material.

The SrO–ZrO<sub>2</sub> system has attracted the interest of researchers since the 1950s. At present several chemical compounds existing in this system are known: SrZrO<sub>3</sub>, Sr<sub>2</sub>ZrO<sub>4</sub>, Sr<sub>3</sub>Zr<sub>2</sub>O<sub>7</sub>, Sr<sub>4</sub>Zr<sub>3</sub>O<sub>10</sub> [1]. Strontium metazirconate SrZrO<sub>3</sub> is used in production of ceramics; other compounds of this system are not stable and become hydrated in air. Therefore, henceforth SrZrO<sub>3</sub> will be the object of consideration (we will refer to it as strontium zirconate).

Strontium zirconate was most actively investigated concerning the possibility of its use in magnetohydrodynamic plants. The components of these plants experience the effect of high-temperature (up to 2700°C) high-speed (above 1000 m/sec) gas flow and electromagnetic fields and are in contact with alkaline additive, oxidizing reactants, and zirconium dioxide electrodes [2]. Strontium zirconate proved to be suitable for such service conditions. The properties of strontium zirconate ceramics published in the literature [1–6] are given below.

### Properties of strontium zirconate ceramics

Melting point, °C	2646, 2800
True density, g/cm <sup>3</sup>	5.48, 5.35
Temperature of deformation under load of 0.2 MPa, °C:	
start of softening	1870, 1660
4% compression	2180, 1850
Compressive strength, MPa, at temperature 20°C	490, 210
Bending strength, MPa:	
at temperature 20°C	178
at temperature 1400°C	10
Average TCLE in temperature interval 200–1600°C, 10 <sup>–6</sup> K <sup>–1</sup>	10.6

Specific resistivity, Ω · cm, at temperature:

1000°C	2 × 10 <sup>5</sup> , 3 × 10 <sup>2</sup>
1400°C	2.5 × 10 <sup>3</sup>
1500°C	0.7 × 10 <sup>3</sup> , 0.2 × 10 <sup>2</sup>
1600°C	3.6 × 10 <sup>2</sup>
1700°C	1.6 × 10 <sup>2</sup>

Rate of evaporation in vacuum of 1.3 × 10<sup>–2</sup> Pa

according to Langmuir method,

10<sup>–7</sup> kg/(m<sup>2</sup> · sec), at temperature:

1700°C	34
1800°C	59
1900°C	107
2000°C	180

It can be seen that strontium zirconate has a high melting point (over 2600°C). The absolute evaporativity values of this material in the temperature interval 1700–2000°C are much closer to the values of evaporativity of magnesia spinel than these values in aluminum oxide and significantly less close than magnesium oxide [5]. Strontium zirconate retains insulating properties even at high temperatures (1700–2000°C). The material has high corrosion resistance in alkaline vapors and melts [4].

The drawbacks of this material are its relatively low strength and a rather high TCLE. These properties determine its low heat resistance. However, there are ways to increase it. Paper [7] reports the existence of strontium zirconate refractory with a fragmentary structure which has high heat resistance (the heat resistance for 850°C–water thermal cycles is increased from 2 to 23 cycles).

Owing to their properties, ceramics based on strontium zirconate are used in metallurgy, nuclear energy, in production of refractories, pastes for crucibles for melting metals and alkaline melts, and structural materials in high-temperature furnaces.

<sup>1</sup> D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

Strontium zirconate can be used not only as a refractory material. The studies in [8, 9] investigated the properties of proton conductors based on strontium zirconate, and paper [10] considers a superconducting composite material in which  $\text{SrZrO}_3$  is one of the phases. A study in [11] is dedicated to the development of electrode material based on  $\text{SrZrO}_3$  which can be used at high temperatures and in oxidizing media.

The synthesis of strontium zirconate, similar to zirconates of other alkaline-earth metals, can be implemented in different ways:

- in hydrothermal conditions;
- by firing mixtures obtained by coprecipitation from mixed salt solutions (the technique described in [12], employing a sorbent, can be attributed to the same method);
- melting of respective salts or metal oxides with zirconium dioxide;
- by solid-phase synthesis from respective salts or metal oxides with zirconium dioxide.

There is also a report of the production of zirconates of alkaline-earth metals using the method of self-propagating high-temperature synthesis (RF Patent No. 2079469).

Most often, strontium zirconate is produced by solid-phase synthesis from zirconium dioxide and strontium carbonate. The available data on this subject are sufficiently contradictory [3, 4, 13]. Different researchers registered the beginning of the reaction at different temperatures: at 900°C [3]; below 900°C, but above 700°C [4]; and [13] indicated that the presence of  $\text{SrZrO}_3$  was already registered at temperature 600°C. However, all researchers report that the reaction proceeds at a high speed and virtually ends at 1300°C (the authors of [13] already at 1100°C identified the presence of only  $\text{SrZrO}_3$ ). The reason for the high rate of the solid-phase reaction is the fact that the reaction product does not form a compact layer around zirconium dioxides grains, since it becomes stratified. The layer of the reaction product does not limit the diffusion mass transfer process. The polymorphous transformations of zirconium dioxide (1100°C) and strontium carbonate (920°C) have an activating effect on the course of the reaction, due to the manifestation of the Headwall effect.

A significant increase in the volume of the samples made of the mixture of initial components occurs in solid-phase synthesis of strontium zirconate. This is explained [5, 7, 14, 15] by the difference in the diffusion coefficients of the initial components (the diffusion coefficient of strontium cations is substantially greater than that of zirconium cations). In this case, one can observe the Kirkendall effect (the shift of the reaction front toward strontium oxide) and the Frenkel effect (the formation of diffusion pores in strontium oxide) [15]. Moreover, the difference in the diffusion coefficients of zirconium and strontium cations leads to the fact that the boundaries of synthesized  $\text{SrZrO}_3$  crystals are enriched with strontium oxide [16].

In sintering these molded samples, it is impossible to obtain high-density ceramics even after protracted high-tempe-

perature exposure. Therefore, in order to manufacture dense ceramics, strontium zirconate obtained by solid-phase synthesis is crushed and then molded, and then the molded article is fired up to the sintering temperature (1700°C). The presence of two firing stages with the intermediate crushing stage makes this technology complicated and expensive.

Research was carried out to produce dense ceramics based on strontium zirconate in a single stage [5, 7, 14, 15]. The behavior of the system, when synthesis and sintering coincided in the same stage, was attributed to the difference in the diffusion coefficients of the components, which in the course of interaction form a skeleton consisting of particles of the low-mobility component, and the increase in volume is determined by the intensity of diffusion mass transfer from the more mobile component to the “skeleton” [14]. It is known that when there is inhomogeneity in the density of a sample (for instance, aggregates), sintering proceeds faster in denser areas, i.e., what is known as local compaction takes place [17]. In our case, the skeleton sinters first of all (a “strong skeleton” is formed), and pores persist between compact areas and cannot be removed in the final stages of sintering. In order to obtain a dense material, it is necessary to prevent the formation of a strong hollow skeleton.

The researchers investigating the production of dense strontium zirconate in a single stage identified numerous factors which affect the structure formation. These factors include: deviation from stoichiometry, variations in the firing rate, granulometric composition, duration of batch exposure before molding, and use of various additives and technological binders [5, 7, 14, 15].

The main problem of these studies was the poor reproducibility of the results. This was not the consequence of inaccuracy of the researchers, but the manifestation of the highly non-equilibrium nature of the considered system. With different processes (synthesis and sintering) occurring simultaneously, the system finds itself in an unstable, non-equilibrium state. If the unstable state in such system is followed by multistability, with stable states significantly different in their properties, it is virtually impossible to predict with accuracy the further evolution of this system. Slight influences exercised on such system within the range of its unstable state can lead the system to one or another stable state, which differ significantly in their properties, this being the reason for the poor reproducibility [18]. The goal of a researcher is to identify the unstable state range of the system characterized by multistability and the stable states which differ significantly in properties, and to eliminate the multistability by means of a controlling signal, whose level would exceed the noise (uncontrollable influences) level.

Thus, strontium zirconate is promising for application under high service temperatures (high-temperature heat insulation, crucibles for alkaline melts, etc.), as well as for electrical ceramics. However, there exists a number of problems related to the fact that the two-stage technology is too complicated, and when ceramics is produced in a single stage, the results are not sufficiently stable. The reason for this is the

substantial difference in the rates of diffusion mass transfer of strontium and zirconium cations, which leads to the formation of diffusion porosity and deviation from stoichiometry. Strontium zirconate is a convenient object for studying the peculiarities of the processes which take place when synthesis and sintering of complex oxides coincide in a single stage. Therefore, the investigation of the processes occurring when the synthesis and sintering of  $\text{SrZrO}_3$  proceed in a single stage is of great interest with respect to the properties of these compounds and the use of these results in producing ceramics based on other complex oxides.

## REFERENCES

1. T. Noguchi, T. Okubo, and O. Yonemochi, "Reactions in system  $\text{ZrO}_2 - \text{SrO}$ ," *Am. Ceram. Soc.*, **52**(4), 178 – 181 (1969).
2. *High-Temperature Materials for Magnetohydrodynamic Power Plants* [in Russian], Nauka, Moscow (1983).
3. E. K. Keler and A. K. Kuznetsov, "Synthesis and physicochemical properties of strontium and barium zirconate," *Zh. Prikl. Khim.*, **34**(10), 2146 – 2153 (1967).
4. M. Zborowska, "The preparation and properties of strontium zirconate ceramics for channels of open-cycle MHD generators," *Ceramurgia Intern.*, **6**(3), 99 – 102 (1980).
5. *Ceramics Based on Highly Refractory Oxides* [in Russian], Metallurgiya, Moscow (1977).
6. N. T. Dzhigailo, "The use of yttrium, tungsten, and niobium oxide additives to increase electrical resistivity of ceramics based on strontium zirconate," *Ogneupory*, No. 8, 11 – 13 (1993).
7. V. S. Bakunov and A. V. Belyakov, "Production of refractories with prescribed properties," *Ogneupory*, No. 1, 15 – 17 (1995).
8. N. Sata, M. Ishigame, and S. Shin, "Optical absorption spectra of acceptor-doped  $\text{SrZrO}_3$  and  $\text{SrTiO}_3$  perovskite-type proton conductors," *Solid State Ionics*, **86 – 88**(1), 629 – 632 (1997).
9. F. Krug and T. Schober, "The high-temperature proton conductor strontium zirconate: thermogravimetry of water uptake," *Am. Ceram. Soc.*, **80**(3), 794 – 796 (1997).
10. O. V. Pupysheva, O. A. Shlyakhtin, and V. V. Lennikov, "Production of composites  $\text{BiSrCaCu}_2\text{O}_x + \text{SrZrO}_3$  from highly disperse mixture melts produced by the cryochemical method," *Neorg. Mater.*, **33**(9), 1122 – 1126 (1997).
11. H. W. King, "Electrical resistivity and high temperature stability of mixed perovskite ceramics based on strontium zirconate," *High Temp. Sci.*, **13**(1 – 4), 135 – 147 (1980).
12. S. P. Kudryavtseva and V. M. Gelis, "Production of zirconates of alkaline-earth and rare-earth elements in the form of microspherical granules using a composite sorbent based on VPK ionite and zirconium hydroxide," in: *Proceedings of Second Rus. Conf. on Radiochemistry* [in Russian], Dimitrovgrad (1997), p. 130.
13. G. V. Bois, E. I. Gindin, N. A. Mikhailova, et al., "Reaction of  $\text{ZrO}_2$  with carbonates of alkaline-earth metals," *Neorg. Mater.*, **12**(3), 456 – 460 (1976).
14. V. S. Bakunov, A. V. Belyakov, N. T. Dzhigailo, and R. Ya. Popil'skii, "The possibility of production of dense ceramics based on zirconates of rare-earth metals in a combination of synthesis and sintering," in: *Publ. of D. I. Mendeleev Moscow Chemical Engineering Inst., No. 128* [in Russian], Moscow (1983), pp. 67 – 71.
15. V. S. Bakunov, A. V. Belyakov, and N. T. Dzhigailo, "Heterogeneous diffusion in binary oxide powder mixtures in heating," *Steklo Keram.*, No. 12, 19 – 20 (1997).
16. A. V. Belyakov, "Estimate of diffusion rates in solid-phase reactions of highly disperse oxides," *Steklo Keram.*, No. 7, 22 – 24 (1999).
17. A. B. Belyakov and E. A. Brygina, "Local compactions in sintering of ceramics and reproducibility of structure," *Steklo Keram.*, No. 10, 10 – 13 (1998).
18. A. Yu. Loskutov, "Reproducibility of structure and properties of articles and their description in the context of nonlinear dynamics," *Steklo Keram.*, No. 7, 17 – 20 (2000).